Studies of Electronic Structures for α-Al_2O_3 and $AlPO_4$ by Al-L and O-K Absorption Spectra

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INTRODUCTION

Aluminum atoms in aluminosilicates are coordinated by oxygen atoms in many silicate net-works and have four-, five-, or six-coordinated structure, and sometimes have their mixed coordinated structure, however, it is not so easy to determine the coordination structures. We analyzed the coordination structures of mullite precursors by Al MAS-NMR[1] and XAFS[2], and the results show the existence of the five-coordinated structure in the precursors. But the XAFS spectra by our laboratory XAFS spectrometer was not so distinct. To analyze the structures of mullite and mullite precursors clearly, we measured X-ray absorption spectra for some aluminum silicates and reference samples such as α-alumina α-Al_2O_3 and aluminum phosphate $AlPO_4$, and analyzed the spectra by a molecular orbital calculation method, a DV-Xα method.

RESULTS AND DISCUSSION

The absorption spectra were measured by the spectrometers at UVSOR beamline 7A and at ALS beamline 6.3.2. The UVSOR and ALS beamlines are bend magnet beamlines and the energy range for the UVSOR beamline is 100eV-1500eV, and that for the ALS beamline is 50eV-1000eV. Absorption spectra were obtained by collecting total electrons from the samples.

Al-K absorption spectra of some aluminosilicates and reference samples obtained by the UVSOR beamline are shown in Fig. 1. There are some differences of the spectra from α-alumina having a six-coordinated structure to aluminum phosphate having a four-coordinated structure. However, by the absorption spectra of Al-K for reference samples shown in Figs. 2 & 4 obtained by the ALS beamline, the spectra differences between the reference samples are quite distinct. Figures. 3 & 5 show also distinct differences between the reference samples for O-K edges.

Molecular orbital calculations were performed by using a discrete-variational(DV) Xα method[3]. The basis functions for α-Al_2O_3 were 1s-4p for O and 1s-5p for Al, and for $AlPO_4$ they were 1s-4p for O, 1s-3d for P, and 1s-5p for Al. For numerical Integration sample points of 10000 for α-Al_2O_3 and 13000 for $AlPO_4$ were distributed three-dimensionally in a manner described elsewhere[4]. In the present study, models of $(Al_{14}O_6)^{20+}$, and $(AlO_{16}P_4)^{29-}$ were employed for the calculations of α-Al_2O_3 and $AlPO_4$, respectively. In case of α-Al_2O_3, an aluminum atom is surrounded by 6 oxygen atoms in the first coordination sphere and 13 aluminum atoms in the second sphere, and in case of $AlPO_4$ an aluminum atom is surrounded by 4 oxygen atoms in the first sphere, 4 phosphorous atoms in the second sphere, and 12 oxygen atoms in the third sphere. Using these models the calculated transition probabilities for each transition give good fits with observed spectra in Figs. 2-5. Comparing the result of Tanaka and Adachi[5], the fit between observed and calculated spectra in Fig. 3 is good enough though the model is simpler than that of them in the observed region. The calculation of the Al-K spectra of aluminosilicate samples and the comparison of the results with those obtained from reference samples are in due course.

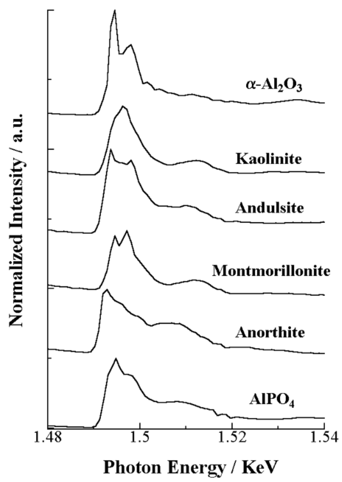

Fig.1 Al K XANES Spectra of a Series of Al Compounds

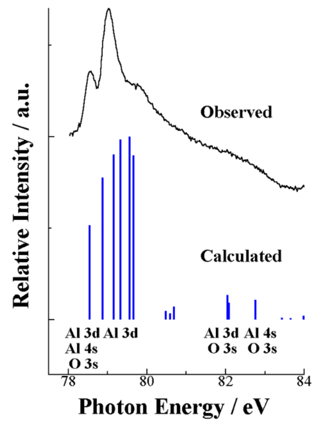

Fig. 2 Observed and Calculated Al-$L_{II,III}$ XANES Spectra of α-Al_2O_3

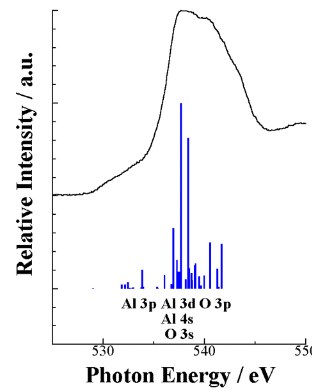

Fig.3 Observed and Calculated O-K XANES Spectra of α-Al_2O_3

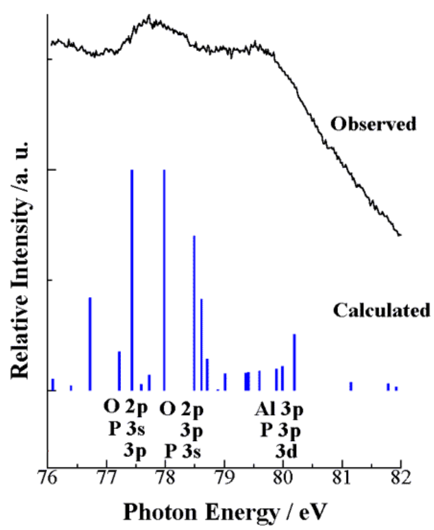

Fig.4 Observed and Calculated Al-$L_{II,III}$ XANES Spectra of $AlPO_4$

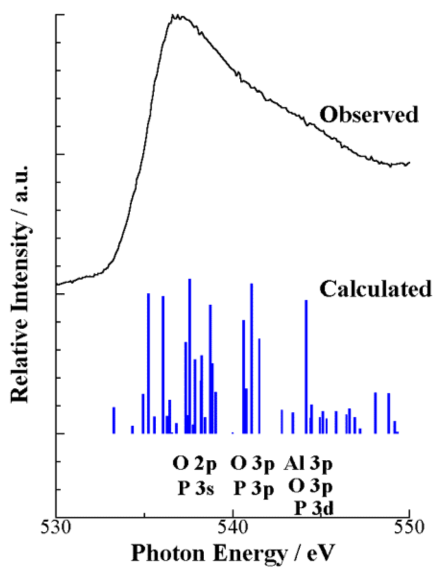

Fig.5 Observed and Calculated O-K XANES Spectra of $AlPO_4$

REFERENCES

1) Y.Ikeda,T.Yokoyama, S.Yamashita, and H.Wakita, Jpn. J. Appl. Phys. Suppl.32, 670(1993).
2) Y.Ikeda,T.Yokoyama, S.Yamashita, T.Watanabe, and H.Wakita, Adv. in X-ray Chem. Anal. Jpn., 26, 211 (1995).
3) D.E.Ellis, H.Adachi, F.W.Averill, Surf.Sci., 58, 497(1976).
4) H.Adachi, M.Tsukada, C.Satoko, J.Phys.Soc.Jpn., 45, 875(1978).
5) I.Tanaka, H.Adachi, Pys.Rev.B, 54, 4604(1996).

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